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GB 1238073  
GB 1177414  
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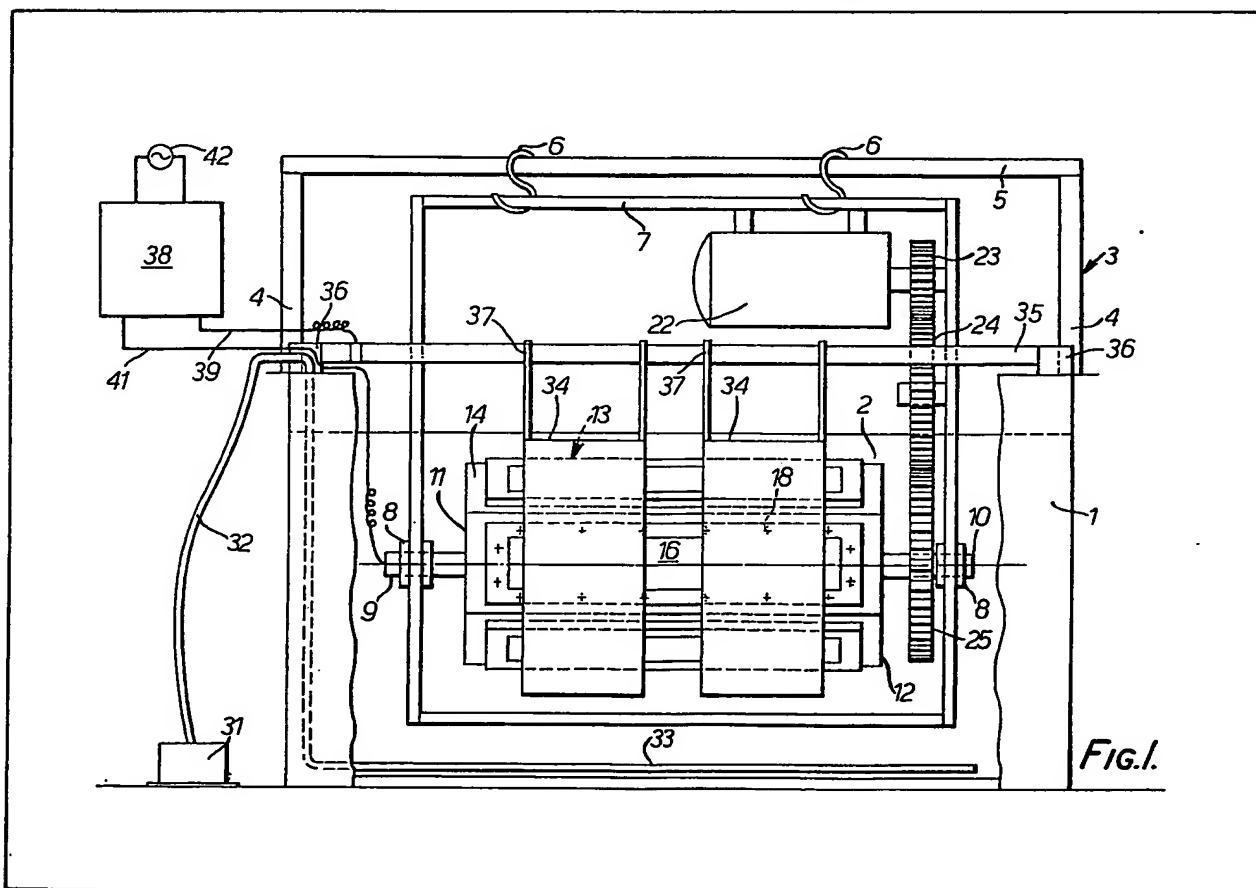
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(54) Processes for the electrodeposition of composite coatings

(57) A process of and apparatus for coating an article (28) with a layer of metal incorporating particles. The article is placed in a barrel (13) together with the particles and the barrel is placed in a plating bath (2) and rotated therein. The barrel has an opening covered by a cover (16) which is pervious to the solution but impervious to the particles. The article is thus flowed over by solution within the barrel which can have a high concentration of particles but there are no particles in the part of the bath outside the barrel. The process may be electroless or electrolytic; in the latter case, the anode (34) is preferably outside the barrel. Electroless coatings of NiP or Ni-B containing diamonds, and electrolytic coatings of Co containing chromium carbide are referred to.



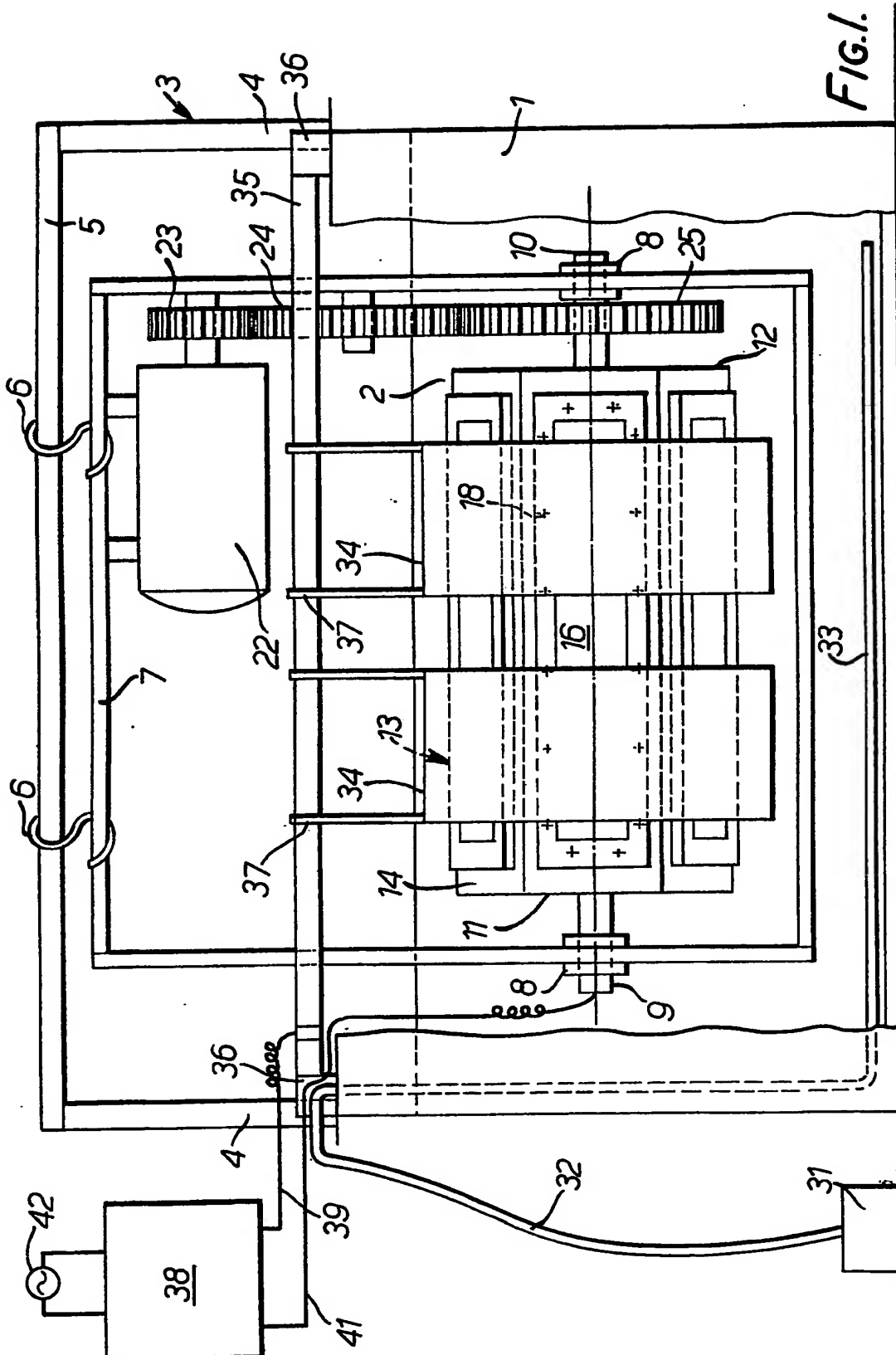
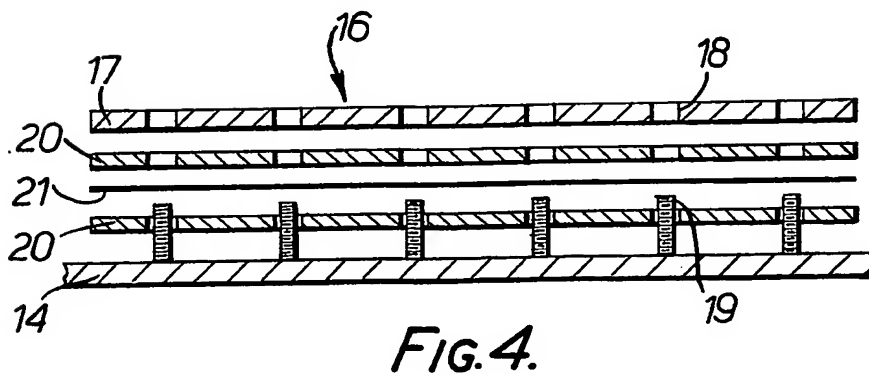
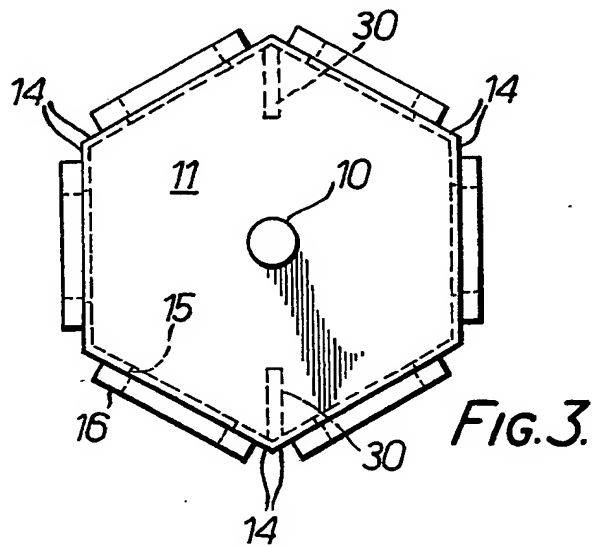
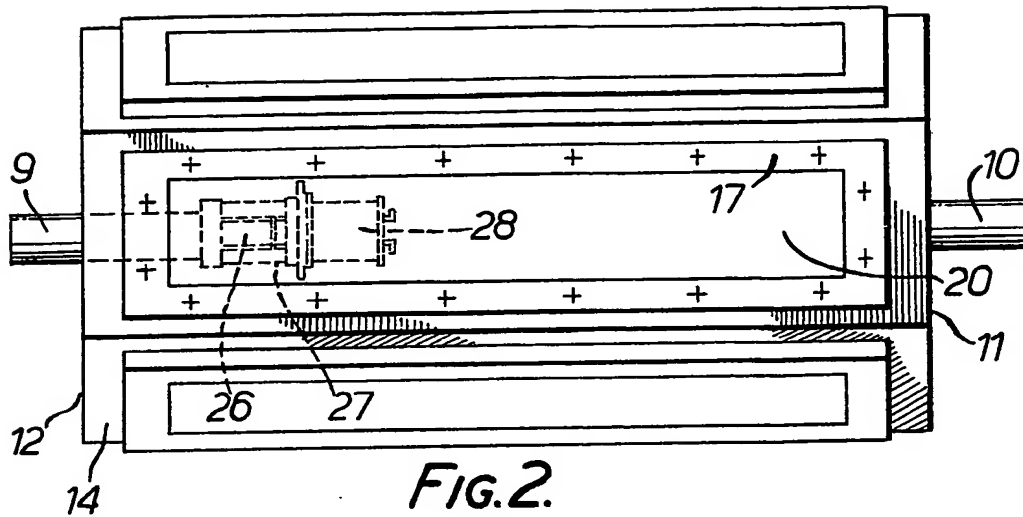


FIG. 1.

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## SPECIFICATION

## Processes for the electrodeposition of composite coatings

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This invention relates to processes and apparatus for the electrodeposition of composite coatings which consist of a metal matrix containing particles, in which processes the particles are co-deposited with the metal from a solution in which the particles are insoluble. The invention is primarily concerned with the electrodeposition of coatings incorporating ceramic particles but the particles may be of cermet or metal. Such coatings may be used for various purposes including wear and abrasion resistance, corrosion and oxidation resistance and improvement in coefficient of friction (lubricity) and anti-fretting and anti-galling properties. In certain cases the coatings themselves may constitute the final product after removal of a substrate. The process comprising electrodeposition in a bath containing insoluble particles dispersed in the bath, the particles being co-deposited with the metal deposited from the bath. The process and apparatus of the invention may be used for electroless deposition but are particularly applicable to electrolytic deposition.

In British Patent No. 860 291 it is proposed to remove electrolyte containing particles from the bottom of the bath and to reintroduce this electrolyte to the top of the bath so that the particles fall through the bath under gravity; the article which is being coated and which forms the cathode is rotated about a generally horizontal axis so that the falling particles settle on the parts of the particle which are uppermost for the time being. It has been found that this system does not provide an even coating, particularly on parts which are of irregular shape. British Patent No. 1 218 179 describes a process in which the article is suspended without movement in a bath and the particles are maintained in suspension in the bath by circulating the solution, gas being admitted to the container to produce a generally upward flow of solution and gas in the vicinity of the surface on which deposition is occurring. Another construction is described in British Patent No. 1 329 081 in which the solution is agitated by movement generally up and down of a generally horizontal perforated agitator in the solution below the part being coated. Both these arrangements have proved extremely satisfactory in use but both require large volumes of solution and particles, and this is expensive. In addition, considerable energy is required to maintain the large volume of the bath homogeneous.

According to one aspect of the present invention, a process of coating an article with a layer of metal incorporating particles comprises placing the article and particles within a hollow barrel, immersing the barrel in a plating solution, at least part of the wall of the barrel being impervious to the particles but pervious to the solution, rotating the barrel about a horizontal axis or an axis which is inclined to the horizontal, and co-depositing metal and particles on to the article. Thus, in addition to the turbulence which will be caused by rotation of the barrel, there will also be

circulation of the particles which will be falling under gravity and being carried upwardly again by rotation of the barrel. With this construction it is possible to employ a small quantity of particles and a high rate of inclusion of particles is obtained. The reduction in particle inventory is particularly advantageous where valuable particles such as diamond particles are employed.

To improve circulation of the particles, it is preferred for the barrel to contain paddles rotating therewith, one advantageous form of paddle being axially extending ribs on the interior surface of the barrel. In most cases the article to be plated will be rigidly supported within and from the barrel, but advantages may be obtained in certain cases by supporting the article separately from the barrel so that the article is held stationary or rotates about the axis of rotation of the barrel or another axis at a speed which is different from the speed of rotation of the barrel. In an alternative arrangement the interior surface of the barrel is conductive and is connected into the plating circuit and the part or parts to be plated are loose within the barrel so that they tumble as the barrel rotates.

Where the process is used for electroless plating, the solution will be of appropriate composition, for example a nickel-phosphorus or a nickel-boron electroless plating solution with diamond particles in the barrel. Where the process is used for electrolytic plating, the solution will be of appropriate composition, for example a cobalt plating solution with chromium carbide particles in the barrel, and the process will include passing an electric current between an anode in the solution and the article.

By use of the process, it is possible to cause a stream of solution heavily loaded with particles to flow gently over the surface to be plated without stagnation occurring. The heavy loading is achieved in a restricted area, i.e. within the barrel, while there is a larger volume of solution whose characteristics, e.g. temperature, concentration and homogeneity, can more easily be maintained constant than could a smaller volume. The space outside the barrel can be utilised for such items as heaters, agitators and, in the case of electrolytic plating, anodes which would in the previous processes have been located in the solution containing particles.

According to a second aspect of the invention, apparatus for electroplating an article with a layer of metal incorporating particles comprises a tank containing plating solution; a hollow barrel rotatably supported within the solution, the barrel having a wall at least a part of which is impervious to the particles but pervious to the solution; means for rotating the barrel; and mounting means in the barrel for an article to be plated.

The invention may be carried into practice in various ways but one form of apparatus in accordance with the present invention will now be described by way of example with reference to the accompanying drawings, and in addition two specific examples of the process using the apparatus will now be described. In the drawings:

Figure 1 is a somewhat diagrammatic side elevation of apparatus for performing a process of elec-

trodeposition of composite coatings, part of the tank wall being broken away to show the apparatus within;

Figure 2 is a side elevation of the drum of the apparatus shown in Figure 1 to a slightly enlarged scale;

Figure 3 is an end elevation of the drum shown in Figure 2; and

Figure 4 is an exploded view of one composite closure panel for the barrel.

The apparatus shown in the drawings comprises a tank 1 to contain a bath 2 of electrolyte otherwise referred to as solution. A framework 3 having uprights 4 and a horizontal 5 extends over the bath to support by means of S-hooks 6 a frame 7 which depends into the bath 2 and carries bearings 8 in which trunnions 9 and 10 rotate. The trunnions are attached to the opposite end walls 11, 12 of a hexagonal hollow barrel 13 comprising six walls 14 each of which contains a rectangular aperture 15 closed by a composite cover 16 the construction of which is shown in more detail in Figure 4. Each cover comprises a rectangular frame member 17 having a plurality of holes 18 through which studs 19 attached to the respective wall 14 of the barrel 13 can pass. The frame traps between itself and the wall 14 a sandwich constituted by two outer layers 20 of porous neoprene and an inner layer 21 formed by filter paper. The neoprene layers, which are 3 millimetres thick, have a nominal pore size of 10 micrometres ( $\mu\text{m}$ ) while the filter paper has a nominal pore size of  $2\mu\text{m}$ .

Extending across the open top of the tank 1 are a pair of spaced copper tubes 35 whose ends rest in insulating saddles 36 carried on the upper edges of the end walls of the tank. Suspended from the tubes 35 by copper hooks 37 are four anodes 34. Each anode comprises a titanium basket shaped as a flat panel, cobalt chips contained in the basket and a conventional anode bag enclosing the basket. The tubes 35 are positioned so that two of the anodes hang adjacent to each side of the barrel 13.

The barrel can be rotated by means of an electric motor 22 supported by the upper horizontal of the frame 7 and connected to the trunnion 10 by a gear wheel 23 on the motor output shaft, an idler wheel 24 mounted on an upright of the frame 7, and a gear wheel 25 mounted on the trunnion 10. The barrel contains paddles 30.

As can be seen in Figure 2, the inner end of the trunnion 9 extends axially into the barrel and terminates in a threaded spigot 26 on which can be screwed a mounting jig 27 carrying a part 28 to be coated, in this case a turbine stator blade having platforms at each end.

Direct current can be supplied to the apparatus from a conventional electroplating control system 38 by a first lead 39 connected to each of the tubes 35 and hence to the cathodes 34 and a second lead 41 which passes through the trunnion 9 to the mounting jig 27 and hence to the part to be coated. The control system 38 which includes a rectifier is supplied from the A.C. mains 42.

The apparatus includes an air blower 31 connected by a flexible pipe 32 to a horizontal outlet pipe 33 in

the base of the tank 1, the outlet pipe 33 having a number of apertures in its upper surface so that when the blower 31 is in operation air can be bubbled into the solution.

#### 70 EXAMPLE I

Using the apparatus described, a stainless steel panel two inches (50.8 mm) by one inch (25.4 mm) by one-eighth of an inch (3.2 mm) thick was provided with a composite coating comprising a cobalt matrix including particles of chromium carbide. The tank was filled with a solution comprising 450 grams per litre of cobalt sulphate, 30 grams per litre of boric acid and 2.5 grams per litre of sodium chloride. To 125 litres of this solution contained in the tank was added 10 millilitres of Canning's anti-pit liquid.

The panel to be coated was given a pretreatment comprising immersion in a cyanide cleaner for two minutes followed by a water-rinse, etching by immersion for 30 seconds in a 50% sulphuric acid followed by a water rinse, and a nickel strike by plating in a nickel bath for three minutes at a current density of 3.9 amps per square decimetres. The panel was secured in the plating barrel in the manner described for the stator blade 28 shown in Figure 2 and the panel was connected to a cathode contact. Sufficient chromium carbide powder with a mean particle size of 2 to  $5\mu\text{m}$  was added to the barrel in an amount to provide 2500 grams per litre of barrel capacity and the opening in the barrel through which the panel to be coated and the powder were admitted was closed by the attachment of a cover 16. The barrel was then completely submerged in the solution in the tank and was rotated at three revolutions per minute while composite plating took place at a voltage of between 2.5 and 3 volts with a current density of approximately 2.7 amps per square decimetre. The solution temperature was maintained at  $50^\circ\text{C}$  and the solution had a pH of between 4.5 and 5. After plating had proceeded for a time sufficient to give a thickness of plating of 0.05 mm, plating was stopped and the panel was examined. It was found that the panel had been given a tenacious coating having an even distribution of particles with a particle content of approximately 28.9% by weight and 35.2% by volume. The barrel capacity was 6 litres.

A series of experiments using the process and apparatus described in the aforementioned British Patent No. 1 218 179 but otherwise using the conditions of the Example set out above and with a progressively increasing loading of particles has indicated that the proportion of particles in the coating increases little, if at all, as the loading rises above 400 grams per litre at which level the proportion was found to be about 23% by weight. A series of experiments using the apparatus shown in Figures 1 to 4 and following the procedure set out in the Example above produced the following results:

	Bath loading grams per litre	Particle Inclusion (weight %)
	400	17.
	500	20
5	600	22.6
	700	23.1
	1000	24.9
	1500	26.5
	2500	28.9
10	3000	33.2

It will be seen that the limit which occurs with the process described in British Patent No. 1 218 179 does not occur with the process described in the present specification.

#### EXAMPLE II

The apparatus described was used for electrolessly plating a stainless steel panel two inches (50.8 mm) by one inch (25.4 mm) by one-eighth of an inch (3.2 mm) thick with a composite coating comprising a nickel-phosphorus matrix including diamond particles. The tank was filled with a proprietary electroless nickel-phosphorus plating solution known as Niklad-794 and sold by Lea Manufacturing Limited of Buxton, Derbyshire, England. The bath was made up of equal parts of 794A diluted to 80 millilitres/litre and 794B diluted to 150 ml/l.

The panel to be coated was given the same pre-treatment as in Example I and secured in the barrel in the same way. Sufficient diamond powder was added to the barrel to provide 35 gms/l of barrel capacity, that is more than four times the nickel content of the same quantity of solution. The barrel was then closed and completely submerged in the solution in the tank and was rotated at three revolutions per minute. To initiate the electroless deposition, a voltage of 2 volts was established between the article and the anodes for between five and ten seconds and was then switched off. Electroless deposition was allowed to continue for one hour. It was found that the panel then carried a homogeneous and tenacious deposit 20  $\mu$ m thick and containing between 20 and 25% by volume of diamond powder in a nickel-phosphorus matrix. This may be compared with between 15 and 20% by volume of diamond powder contained in deposits using similar conditions but using the process and apparatus described in the aforementioned British Patent No. 1 218 179.

#### CLAIMS

1. A process of coating an article with a layer of metal incorporating particles, the process comprising placing the article and particles within a hollow barrel, immersing the barrel in a plating solution, at least part of the wall of the barrel being impervious to the particles but pervious to the solution, rotating the barrel about a horizontal axis or an axis which is inclined to the horizontal, and co-depositing metal and particles on to the article.
2. A process as claimed in Claim 1 in which the plating solution is an electroless plating solution.
3. A process as claimed in Claim 2 in which the plating solution is a nickel-phosphorus or a nickel-boron plating solution and the particles are diamond.
4. A process as claimed in Claim 1 in which the

plating solution is an electrolytic plating solution, and the process includes passing an electric current between an anode in the solution and the article.

5. A process as claimed in Claim 4 in which the anode is located outside the barrel.

6. A process as claimed in Claim 4 or Claim 5 in which the particles are chromium carbide particles and the solution is a cobalt plating solution.

7. A process as claimed in Claim 4 or Claim 5 or Claim 6 in which the barrel contains at least two kilograms of particles per litre of barrel capacity.

8. A process as claimed in any of the preceding claims in which the barrel contains paddles rotating therewith.

9. A process as claimed in Claim 8 in which the paddles are axially extending ribs on the interior surface of the barrel.

10. A process as claimed in any of the preceding claims which includes rigidly supporting the article within and for rotation with the barrel prior to immersion of the barrel in the solution.

11. A process as claimed in any of the preceding claims in which the barrel is rotated at a speed not greater than four revolutions per minute.

12. A process as claimed in any of the preceding claims in which the particles have a mean particle size of between one and ten micrometres.

13. Apparatus of electroplating an article with a layer of metal incorporating particles, the apparatus comprising: a tank containing plating solution; a hollow barrel rotatably supported within the solution, the barrel having a wall at least a part of which is impervious to the particles but pervious to the solution; means for rotating the barrel; and mounting

- means in the barrel for an article to be plated.

14. Apparatus as claimed in Claim 13 which includes an anode in the tank; and electrical means for applying a potential between the anode and the article.

15. Apparatus as claimed in Claim 14 in which the anode is outside the barrel.

16. Apparatus as claimed in Claim 13 or Claim 14 or Claim 15 in which the barrel has an impervious body having at least one opening closed by a cover which is impervious to the particles but pervious to the solution.

17. Apparatus as claimed in Claim 16 in which the cover comprises a layer of filter paper between two layers of porous polymeric material having a larger pore size than the filter paper.

18. Apparatus as claimed in Claim 17 in which the polymeric material is neoprene.

19. Apparatus as claimed in any of Claims 13 to 18 in which the barrel contains paddles rotatable therewith.

20. Apparatus as claimed in Claim 19 in which the paddles are axially extending ribs on the interior surface of the barrel.

21. Apparatus for electroplating an article with a layer of metal incorporating particles, the apparatus being substantially as described herein with reference to the accompanying drawings.

22. A process of electroplating an article with a layer of metal incorporating particles, the method being substantially as described herein with refer-

ence to the foregoing Example I.

23. A process of coating an article with a layer of metal incorporating particles, the method being substantially as described herein with reference to the foregoing Example II.

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